Indian J. Phys. **78A** (1), 67-69 (2004)

Nanomaterials–2003

AN INTERNATIONAL JOURNAL

IJP

Preparation of barium ferrite nanoparticles from a nonaqueous precursor

P Deb[1]*, S Ghosh[1], A Basumallick[1] and N R Bandyopadhyay[2]

[1]Department of Metallurgy, Bengal Engineering College (D U), Howrah-711 103, India

[2]Dr. M. N Dastur School of Materials Science & Engineering Bengal Engineering College (D.U.), Howrah-711 103, India

Abstract : Nanosized barium ferrite particles were prepared from a nonaqueous precursor by thermolysis. The precursor medium comprise calculated amount of stearic acid iron(III) nitrate and barium carbonate. Thermolysis of the precursor at 125°C, causes precipitation of Fe_2O_3 and BaO in the stearic acid medium. The precursor medium gradually turns viscous as function of thermolysis time. Heat treatment (400°C for 1 hr) of powder precipitates obtained by centrifugation of tetrahydrofuran (THF) treated thermolysed precursor yields nanosized barium ferrite particles. The chemical and thermal characteristics of the powder precipitates were studied with the aid of Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). X-Ray diffraction (XRD) studies carried out on the heat treated powder sample reveal the presence of nanosized barium ferrite particles. Results of the XRD line profile analysis and transmission electron microscopic (TEM) analysis show that the average size of the barium ferrite particles is 30 nm.

Keywords : Nanoparticles, barium ferrite, nonaqueous, thermolysis, precursor

PACS Nos. : 75.50.Tt, 61.46.+w, 68.37.Lp

1. Introduction

Nanocrystalline magnetic materials have emerged as a new class of permanent magnet material. In particular, nanoparticles of M-type barium ferrite have received a great deal of attention in the last few years [1] due to their many potential applications. They find applications in motors based on permanent magnets, as static applications such as loud speakers, where low demagnetization fields are required, or when large anisotropic blocks are needed. They are also used in small household appliances. They can also be used as digital recording media for audio and video, and for storing data on hard or floppy disks [2]. Due to their easy magnetization direction, which remain perpendicular to the plane of the platelets, they can be used as perpendicular magnetic recording media [3,4]. Their development is at present restricted by the difficulty of obtaining ultrafine (nanosized) particles of barium ferrite with narrow size distribution for low media noise. In this regard, recently attention has been focused on materials obtained by "gentle chemistry'. This chemical procedure is characterized by a complete and homogeneous mixing of the initial compounds at the molecular or atomic level followed by thermal treatment at lower temperatures compared to the conventional methods. As a result, the synthesized compounds are characterized by their small particle sizes, high homogeneity and stoichiometry that could not be achieved at high temperatures [5–7]. Therefore, in the present work, we report a simple and versatile route for preparing $BaFe_{12}O_{19}$ nanoparticles from a homogeneous nonaqueous precursor medium.

* Corresponding Author

2. Materials and methods

A homogeneous precursor comprising stearic acid (12.20 gm), barium carbonate (0.79 gm) and iron(III) nitrate (19.41 gm) were prepared by melting the reagents. All the reagents used for the experiment were of analytical grade. Initially, stearic acid was melted at 72°C to which $Fe(NO_3)_3.9H_2O$ was added slowly with continuous stirring. When iron(III) nitrate dissolves completely, addition of $BaCO_3$ was made with continuous stirring. The temperature of the homogeneous solution so formed was raised to 125°C and thermolyzed for nearly two hours till the evolution of NO_2 and CO_2 fumes was ceased. A reddish brown viscous mass was formed which was cooled at room temperature and then treated with 75 ml of tetrahydrofuran (THF). The resulting solution was stirred intensely for 30 mins and powdery precipitates from the solution was recovered by centrifugation. The precipitates so obtained were then dried at 70°C for 36 hrs in an air oven. The as prepared powder precipitates were

characterized by DSC and FTIR. The powder precipitates heat treated at 400°C for 1 hr were characterized by XRD and TEM.

3. Results and discussion

The thermal characterization of stearic acid and the as prepared powder sample were accomplished by the aid of DSC studies. All the experiments were carried out in static air atmosphere at a heating rate of 10°C/min.

Figure 1(a) represents the DSC plot of stearic acid. The plot exhibits a sharp endothermic peak at 57.5°C, which corresponds to the melting of stearic acid [8]. The strong exothermic peak observed in the temperature range 185–290°C corresponds to the decomposition and subsequent oxidation of stearic acid [8]. Figure 1(b) represents the DSC plot of the as prepared powder sample. The plot clearly shows that the melting peak as obtained in case of stearic acid has disappeared completely. This suggests that THF acts here as an organic solvent. THF dissolves and removes excess stearic acid and low melting undesirable organic compounds from the precipitates during centrifugation. The strong exothermic peak in the range of 170–375°C can be assigned to the decomposition and subsequent oxidation of the attached organic matter and liberation of nanosized $BaFe_{12}O_{19}$ particles from the precipitates.

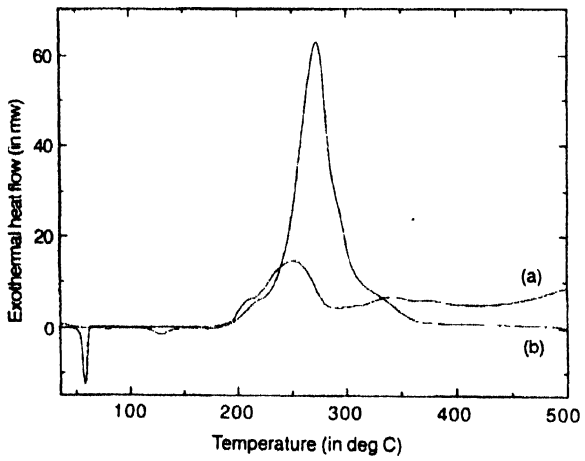

Figure 1. DSC plots of (a) stearic acid and (b) as prepared powder sample.

The chemical and compositional characteristics of the as prepared powder precipitates were analyzed by FTIR spectroscopy. Figure 2 represents FTIR spectrum of the powder particles in KBr solution. The spectrum shows characteristic bands with the peaks at 424.30, 690.50, 810 and 1122.50 cm^{-1}. The peak values were close to those shown in the literature for the Fe-O system [9]. Presence of C-NO_2 (nitro compounds) and N-NO (nitrites) in the precipitates is indicated by the peaks observed at 1380, 1602.70 and 1697.20 cm^{-1} respectively [9]. The peaks observed at 2850.60, 2920.00 and 2373.30 cm^{-1} corresponds to the C-H vibrations and OH deformation vibrations of the residual stearic acid [10]. Therefore, from the above spectroscopic observation we conclude that powder precipitate samples contain nitro compounds, nitrites and residual stearic acid.

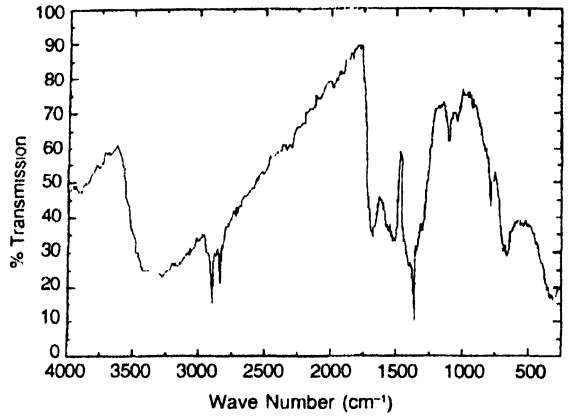

Figure 2. FTIR spectrum of as prepared powder precipitates

XRD studies were carried out on the as prepared precipitates and powder samples heat treated isothermally for 1 hr at 400°C The XRD pattern of both the samples were recorded using CuK_α radiation. Figure 3 shows the XRD pattern of the as prepared powder sample alongwith the sample heat treated at 400°C for 1 hr. The XRD pattern of the as prepared precipitate does not exhibit any significant crystalline peak. This indicates that $BaFe_{12}O_{19}$ so formed during sample preparation remains entrapped in an organic layer. This corroborates the inferences drawn from the FTIR spectroscopic studies. Heat treating the sample in air at 400°C for 1 hr causes decomposition of the organic layer and simultaneous liberation of $BaFe_{12}O_{19}$. A pattern decomposition procedure using a pseudo-Voigt profile shape function [11] and subsequent single line analysis based on equivalent Voigt representation [12] was used for the determination of crystalline size and microstrain in the crystallites. The volume weighted mean crystalline size of $BaFe_{12}O_{19}$ has been found to be 30 nm for the sample heat treated at 400°C for 1 hr and the corresponding lattice strain is 0.27%.

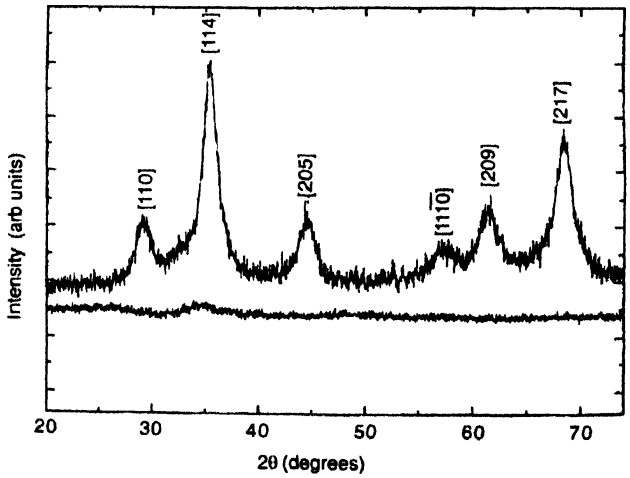

Figure 3. XRD pattern of the as prepared powder precipitates and powder precipitates heat treated at 400°C for 1 hr.

Figure 4 represents the TEM micrograph of the sample heat treated at 400°C for 1 hr. A careful examination of the TEM

micrograph of the sample reveals the presence of nonspherical agglomerates of fine particles. The average particle measured from the TEM micrograph is 42 nm. The difference between the particle sizes estimated from the XRD and TEM micrograph may be attributed to the unavoidable error in particle size measurements (in case of TEM) restricted to a limited number of particles focussed under the electron microscope.

Figure 4. TEM micrograph of the sample heat treated at 400°C for 1 hr

4. Conclusions

The conclusions drawn from the present investigations are summarized below:

Nanosized $BaFe_{12}O_{19}$ particles of average size 30 nm can be prepared by heat treating the precipitates obtained from a nonaqueous homogeneous solution of stearic acid, iron(III) nitrate and barium carbonate. DSC and FTIR spectroscopic studies indicate that the as prepared powder precipitate contains Fe-O system, nitro compounds, nitrites and residual stearic acid. The XRD line profile analysis and TEM micrograph confirm the presence of nanosized $BaFe_{12}O_{19}$ particles in the sample.

References

[1] J Dufour, R Latorre, C Negro, E M Alcala, A Formoso and F Lopez-Mateos *J. Magn Magn. Mater.* **172** 308 (1997)

[2] D E Speliotis *J. Appl. Phys.* **61** 25 (1987)

[3] K Kakizaki, H Sano, M Fujita and N Hiratsuka *J. Magn. Soc. Japan* **17(s2)** 29 (1993)

[4] M C A Mathur, S Datta, G W D Spratt and M Kryder *Advances in Ferrites* in *Proc. ICF-5* (New Delhi · Oxford and IBH, New Delhi) (1989) pp 869-873

[5] P Deb, A Basumallick, P Chatterjee and S P Sengupta *Scripta Mater.* **45** 341 (2001)

[6] P Deb and A Basumallick *J Mater Res.* **16** 3471 (2001)

[7] E Uzunova, D Klisurski, I Mitov and P Stefanov *Chem Mater* **5** 576 (1993)

[8] N Irving Sax and R J Lewis Sr *Hawley's Condensed Chemical*, 11th ed (New Delhi CBS Publication) (1990) p1091

[9] M K Wilson *Infrared and Raman Spectroscopy* chap 3, **Vol 2**, in F C Nachod and W D Phillips *Determination of Organic Structures by Physical Methods* (New York : Academic) p181 (1962)

[10] J R Dyer *Application of Absorption Spectroscopy of Organic Compound* (New Delhi · Prentice Hall of India) 22 (1987)

[11] S Enzo, G Fagherazzi, A Benedetti and S Polizzi *J. Appl. Cryt.* **21** 536 (1988)

[12] Th H De Keijser, E Mittemeijer and H C F Rozenda *J Appl. Cryst.* **16** 309 (1983)